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Publication number: **0 488 550 A1**

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## EUROPEAN PATENT APPLICATION

21 Application number: 91310470.9

51 Int. Cl.5: **C08K 5/00, //(C08K5/00,5:13,  
5:13,5:37)**

22 Date of filing: 13.11.91

30 Priority: 30.11.90 US 621173

43 Date of publication of application:  
03.06.92 Bulletin 92/23

64 Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

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54 Thermal stabilizers.

57 Stabilizer compositions comprising a) at least two hindered phenols, one of which is less sterically hindered than the other and b) sulfide, when admixed with polymers, provide polymeric additives which improve the physical and mechanical properties of polymer matrices to which they may be added.

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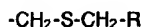
This invention is concerned with compositions for stabilizing polymeric additives, stabilized polymeric additive compositions and products which include stabilized polymeric additives. The polymers of particular interest are butadiene copolymers and acrylic and methacrylic copolymers.

Polymers such as those prepared from methacrylate-butadiene-styrene ("MBS") monomers and polymers predominantly based on acrylic and methacrylic -(meth)acrylic- ester monomers, are routinely employed as additives in polymeric matrices to provide products with improved impact properties. MBS polymers, however, are prone to thermal and oxidative degradation at elevated temperatures. (Meth)acrylic polymers, such as acrylic impact modifiers (herein referred to as "AIMS"), are prone to thermal and oxidative degradation, although to a lesser degree than MBS polymers. This tendency of MBS and AIMS polymers to degrade at elevated temperatures reduces the ability of these polymers to impart improved impact strength in polymer matrices of acrylics, polyamides, and other engineering resins, as well as in blends which require relatively high processing temperatures.

MBS and AIMS polymers employed as additives in polymeric matrices are routinely treated with stabilizers to protect them against thermal and oxidative degradation. However, these stabilizers may cause polymers to lose impact strength and develop coloured impurities in the polymer matrix as a byproduct of their antioxidant action.

This invention is therefore directed to the provision of improved stabilizers for polymers such as MBS and AIMS and to polymeric products of improved physical and mechanical properties that employ the polymers which incorporate these improved stabilizers.

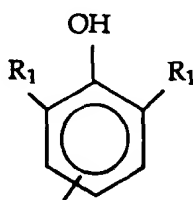
The stabilizer compositions of the invention can be employed with a variety of polymers (but of especial interest are MBS, acrylate-butadiene, acrylonitrile-butadiene-styrene, styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, MBS and AIMS copolymers, AIMS polymers, for example core-shell polymers in which the core and shells predominantly contain (meth)acrylic polymers or copolymers, and the like) to provide polymeric additives which show surprising improvement in thermal degradation and oxidation resistance. The stabilizers of this invention comprise: 1) sulfide having one or more of the following sulfide groups:



wherein R is an alkyl group of from 1 to 20 carbon atoms or an alkyl alkanoate, of the formula:

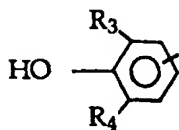


and n is 0, 1 or 2; or 2,4-bis(n-octylthiol)-6-(4'-hydroxy-3',5'-di-tert-butylanilino)-1,3,5-triazine, and 2) sterically hindered phenol containing one or more sterically hindered phenol groups having the formula (1):



(I)

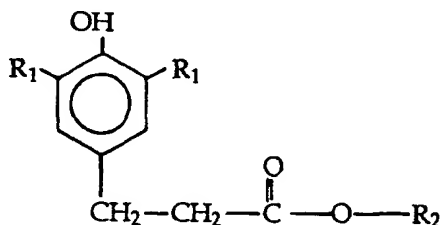
wherein R<sub>1</sub> represents branched chain alkyl, and 3) phenol less sterically hindered than phenol (2) and containing one or more sterically hindered phenol groups having the formula (II):



(II)

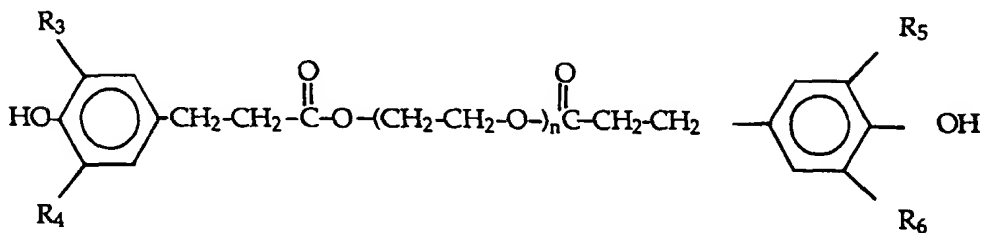
10 wherein R<sub>3</sub> is hydrogen or (C<sub>1</sub>-C<sub>4</sub>)-alkyl and R<sub>4</sub> is branched chain alkyl. In the above formulae (I) and (II) and elsewhere in this disclosure, the line through the phenol groups (i.e. "—") indicates that another radical is attached to the benzene ring. The nature of this radical varies in the many such materials available

15 commercially as stabilisers. In preferred an alkyl sulfides R is alkyl of from 7 to 11 carbon atoms. Preferred a sterically hindered phenols (2) are those of the formula (III):



(III)

30 wherein R<sub>1</sub> is a branched chain alkyl, and R<sub>2</sub> is an alkyl of at least four carbon atoms. Preferred less sterically hindered phenols (3) are those of the formula (IV):



(IV)

50 wherein n is an integer from 1 to 10; R<sub>3</sub> and R<sub>5</sub> are hydrogen or (C<sub>1</sub> to C<sub>4</sub>)-alkyl; and R<sub>4</sub> and R<sub>6</sub> are branched chain alkyl (preferably as later defined as preferred for R<sub>1</sub>). Such a phenol is ethylene bis-(oxyethylene)bis (3-*tert*-butyl-4-hydroxy-5-methylhydrocinnamate.

55 The stabilizer of the invention can be incorporated into polymers to make polymeric additives. These polymeric additives can be employed in polymer matrices to provide polymeric products having improved physical and mechanical properties. The polymeric products may be produced by admixing the additive into a polymer matrix, and then molding the polymer matrix to provide an improved polymeric product.

The sterically hindered phenol (2) preferably comprises from about 5 to 40% of the three component

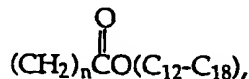
stabilizer composition, and more preferably from about 8 to 33%, the less sterically hindered phenol preferably comprises from about 10 to about 70% of the three component stabilizer composition, and more preferably from about 15 to 33%, and the sulfide preferably comprises about 15 to about 80% of the three component stabilizer composition, and more preferably from about 33 to 73%.

5 In the sterically hindered phenols (2) preferred groups  $R_1$  are branched chain alkyl of from 4 to 12 carbon atoms such as tert-butyl; 2,2-dimethylpropyl; 1-methylpropyl; sec-propyl; 1,2,2-tri-methylpropyl; 2-methylpropyl, 1,2-dimethyl-2-ethylbutyl, and the like. These phenols are exemplified by compositions such as octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,2-propanediyl 3,5-bis (1,1-dimethylethyl)-4-hydroxybenzenepropanoate, 1,3,5-tris(4'-hydroxy-3',5'-di-t-butyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)trione, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl-5-triazine-2,4,6, (1H,3H,5H)-trione, 2,2-bis[4-(2-(3,5-di-t-butyl-4-hydroxy cinnamoyloxy)) ethoxyphenyl] propane, hexamethylene bis (3,5-di-tert-butyl-4-hydroxy hydrocinnamate), thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy hydrocinnamate, N,N'-hexamethylene bis (3,5-di-tert-butyl-4-hydroxy hydrocinnamide, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl)benzene and the like.

10 In the less sterically hindered phenols (3)  $R_4$  is preferably a branched chain alkyl as previously defined above as preferred for  $R_1$  and/or  $R_3$  is preferably hydrogen or straight chain alkyl, of from 1 to 4 carbon atoms. These phenols are exemplified by compositions such as ethylene bis(oxyethylene)bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate), 2,2'-methylene bis (4-methyl-6-t-butyl phenol), octadecyl 3-methyl, 5-t-butyl-4-hydroxy hydrocinnamate, 4,4'-thiobis-(6-tertiarybutyl-o-cresol).

20 In the sulfides of this invention preferred alkyl groups R have 1 to 11, more preferably 7 to 11, carbon atoms and preferred alkyl alkanoate groups R are

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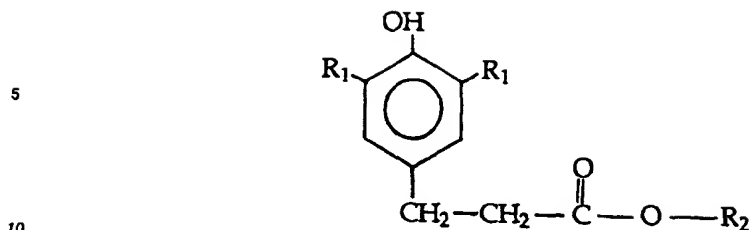
30 wherein n 0, 1 or 2; or the sulfide comprises 2,4-bis(n-octylthiol)-6-(4'-hydroxy-3',5'-di-tert-butylanilino)-1,3,5-triazine. Preferred lower alkyls of from 7 to 11 carbon atoms include heptyl, octyl, nonyl, decyl and undecyl; and another preferred class of alkyl groups R are branched chain lower alkyls of from 3 to 11 carbon atoms such as tert-butyl, 2,2-dimethylpropyl, 1-methylpropyl, sec-propyl, 1,2,2-tri-methylpropyl, 2-methylpropyl, 1,2-dimethyl-2-ethylbutyl, and the like. In the broadest aspect however, alkyl includes lower alkyls of from 1 to 20 carbon atoms (i.e.  $C_1$ - $C_{20}$ ), such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, pentadecyl, icosyl, and the like; and branched chain alkyls of from 3 to 20 carbon atoms (i.e.  $C_3$ - $C_{20}$ ), such as such tert-butyl, 2,2-dimethylpropyl, 1-methylpropyl, sec-propyl, 1,2,2-tri-methylpropyl, 2-methylpropyl, 1,2-dimethyl-2-ethylbutyl, and the like. Examples of suitable sulfides include, but are not limited to dilaurylthiodipropionate, pentaerythritol tetrakis (octyl thiopropionate), distearyl thiodipropionate, dimyristyl thiodipropionate, pentaerythritol tetrakis ( $\beta$ -laurylthiopropionate), 2,4-bis (n-octylthio)-6-(4'-hydroxy-3',5'-di-tert-butylanilino)-1,3,5-triazine, trimethylolpropanetris(octylthiopropionate), trimethylolethane tris(octylthiopropionate) ethylene glycol bis (laurylthiopropionate), and didodecylmonosulfide, and the like.

45 A surfactant may be included in the stabilizer composition to enable an emulsion of the composition to be provided. Examples of suitable surfactants are those which are thermally stable over 200 °C-350 °C; most preferably, sodium dodecylbenzene sulfonate; and the amount of surfactant typically constitutes 5 to 25% (by weight) of the stabilizer emulsion, depending on the specific properties of the surfactant.

In the preferred sterically hindered phenols having the following formula (III):

50

55



(III)

15  $\text{R}_1$  is as set out above and  $\text{R}_2$ , which may be alkyl of at least four carbon atoms, is preferably ( $\text{C}_4$ - $\text{C}_{30}$ )-alkyl such as butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, icosyl, triacontyl and the like, and more preferably ( $\text{C}_{16}$ - $\text{C}_{20}$ )-alkyl. These phenols are exemplified by octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate.

Phenols described above may be manufactured by methods well known in the art, such as acid- or metal-catalyzed alkylation, or thermal alkylation, and the like, as is shown in Encyclopedia of Chemical Technology, Kirk-Othmer, Vol.2, 3rd Ed., pages 65-66.

By "polymeric additive", as used herein, we mean a polymeric composition that is useful as an additive to other polymeric compositions. The polymeric additives of the invention may be prepared by various methods such as by forming a stabilizer mixture of: sterically hindered phenol(s) of formula (I) or (III) above, less sterically hindered phenol(s) of formula (II) or (IV) above, and sulfide, and adding that stabilizer mixture to a polymer to provide a stabilized polymeric additive.

A variety of polymers may be treated with the stabilizer mixtures of the invention to provide polymeric additives. For example, polymers such as acrylonitrile-butadiene-styrene, styrene-butadiene-styrene block copolymers, styrene with a methacrylate, or maleate, or fumarate, or maleate and fumarate, an olefin copolymer with an acrylate, an olefin copolymer with a methacrylate or maleic anhydride followed by functionalization of the anhydride, and the like may be treated with the stabilizers of this invention to provide polymeric additives. In particular, MBS and AIMS polymers may be treated with the stabilizers of the invention to provide polymeric additives. These MBS and AIMS polymeric additives have been found to impart surprisingly improved physical and mechanical properties to polymer matrices such as acrylics and nylons.

AIMS polymers (acrylic impact modifiers) refer to (meth)acrylic polymers. MBS polymers refer to methacrylate/butadiene/styrene polymers, especially those of core/shell structure. In the present application, MBS is also used to refer to polymers containing butadiene/alkyl acrylate/alkyl methacrylate/styrene, styrene/copolymerized acid, and the like. Illustrative of such polymers would be butadiene/butyl acrylate/methyl methacrylate, butadiene/butyl acrylate/styrene/styrene/methyl methacrylate, butadiene/ethyl acrylate/methyl methacrylate/methacrylic acid, and the like.

The types of MBS and AIMS polymers which are useful as polymeric additives, in polymeric matrices such as acrylics and nylons, are of the core/shell type. Core/shell type MBS polymers typically have a rubbery core of polymer that contains at least 50 weight percent butadiene, a second stage shell of either styrenic polymers, styrene/methacrylate polymers, or alkyl methacrylate polymers, and an optional third stage shell of either styrenic polymers, styrene/methacrylate polymers, or alkyl methacrylate polymers, with the qualification that the compositions of the second and third shells are not identical. The second and third stage shells also may be crosslinked. Core/shell type AIMS polymers typically have a rubbery core of polymer that contains at least 50 weight percent of an alkyl acrylate or methacrylate polymer or copolymer and one or more outer stages, shells, or layers of (meth)acrylic and other vinyl monomer polymers or copolymers. The core and outer shells may be crosslinked and graftlinked. Other configurations of core/shell type polymers are however possible.

In the case of amide polymers collectively known as nylons, such as polycaprolactam and poly-(hexamethylene adipamide), and the like, impact strength may be improved by reacting an acid or anhydride functionality on the impact-property modifier with an amine group available on the polyamide. Such functionalised modifiers include acrylic rubber/methyl methacrylate-co-unsaturated acid core-shell polymers as taught in US-A-3668274. Preferred are those core-shell modifiers prepared in an emulsion, such as butadiene/styrene/acrylonitrile (ABS) and butadiene-styrene/styrene/methyl methacrylate (MBS),

and butyl acrylate/methyl methacrylate, and those modifiers having reactive acid functionality. Also useful are acrylic impact modifiers polymers having: 1) a rubbery core of alkyl acrylate, and one or more shells of either styrenic polymers, styrene(meth)acrylate copolymers, or alkyl methacrylate polymers, or 2) a non-elastic, hard first stage of alkyl methacrylate, and one or more shells of either styrenic polymers, styrene-(meth)acrylate copolymers, or alkyl (meth)acrylate polymers and copolymers, of which are exemplified in US-A-3808180 and US-A-3985704. A preferred embodiment of the present invention is the use of such additive polymers to improve the impact resistance of nylons; it is especially useful with, but not limited to, the improvement of impact resistance in polycaprolactam and poly(hexamethylene adipamide), using polymers such as acid-functionalised core-shell polymers described above.

The impact-property modifier may also contain another polymer component such as described in EP-A-87307578.2, which is a copolymer of about 50 to about 95 parts of an alkyl acrylate or alkyl methacrylate having from 1 to 8 carbon atoms in the alkyl group, and with from about 5 to about 50 parts of an unsaturated copolymerizable carboxylic acid. It may also further contain a polymer predominantly of methyl methacrylate with little or no copolymerized carboxylic acid. The polymer additive is prepared by incorporating the stabilizer in one or more polymers such as acrylate, methacrylate, styrene with an acrylate, styrene with a methacrylate, a styrene derivative with an acrylate, a styrene derivative with a methacrylate, or maleate, or fumarate, or maleate and fumarate, an olefin copolymer with an acrylate, an olefin copolymer with a methacrylate or maleic anhydride followed by functionalization of the anhydride.

The total amount of stabilizers may generally vary from about 1.0 to about 3.0 percent by weight of the MBS or AIMS polymer in the polymer additives. For a 2% loading (by weight percent) of the stabilizer, octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (hereinafter called "P1") can be from about 0.1 to about 0.8 weight %, ethylene bis(oxyethylene) bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate) (hereinafter called "P2") can be from about 0.2 to about 1.4 weight %, and pentaerythritol tetrakis ( $\beta$ -laurylthiopropionate) (hereinafter called "S") can be from about 0.3 to about 1.6 weight %, all based on weight of the MBS or AIMS polymer. [See Table 3].

The polymeric additives that are produced by treatment with the stabilizers of the invention can be readily employed in a wide variety of polymer matrices to provide polymer products which have improved physical and mechanical properties, such as improved resistance to thermal and oxidative degradation. The polymeric additives can be included in nylon polymers such as poly(hexamethylene adipamide) and related polyamides, poly(p-phenylene sulfides), polysulfones, polyarylates, polystyrene, poly(ether imides), polyimides, poly(glutarimides), poly(phenylene ethers), aromatic polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), polycarbonates, and the like or mixtures thereof. Especially preferred are polycarbonates of bisphenol A. Generally, the additive is blended with the polymeric matrix which is then molded to form a polymer product that has improved physical and mechanical properties.

Analogous to acrylic and nylon matrices, the MBS and AIMS polymeric additives of the invention can be incorporated into other polymer matrices such as those polymers of aromatic polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate) and the like, nylon polymers such as poly(hexamethylene adipamide) and related polyamides, poly(p-phenylene sulfides), polysulfones, polyarylate, polystyrene, poly(ether imides), polyimides, poly(glutarimides), poly(phenylene ethers), as well as various combinations and blends of these.

Polymeric additives, matrices and blends thereof may contain other components which are well known in the art such as toners, lubricants, antioxidants, colorants, ultraviolet stabilizers, hindered amine light stabilizers, impact modifiers, pigments, fillers, fibers, flame retardants, and the like.

The polymeric products which incorporate the polymeric additives of the invention and polymer matrices may be formed, as for example, by injection molding or extruding, into a variety of useful objects and articles such as transportation and automotive parts, computer housings, electrical and electronic parts, telecommunication parts, industrial machine parts, consumer products, power tool housings, food packaging, wire and cable jacketing, filaments, appliance handles and housings, tough films, and the like.

Examples of transportation parts include but are not limited to electrical connectors, wire jackets, emission canisters, light-duty gears for windshield wipers, speedometers, engine fans, radiator headers, brake and power-steering fluid reservoirs, valve covers, mirror housing, and fender extension. Examples of electrical or electronic parts include but are not limited to plugs, connectors, coil forms, wiring devices, terminal block, and antenna-mounting devices. Examples of telecommunication parts include but are not limited to relays, fittings, and contact makers. Examples of industrial machine parts include but are not limited to hammer handles, moving machine parts, unlubricated gears, bearings, anti-friction parts, and a variety of uses in which snap fits, detents, or spring loading is required. Food and textile-processing equipment, pumps, valves, meters, agricultural and printing devices, business and vending machines, and a host of other industrial products all utilize nylons. Examples of consumer products include but are not

limited to ski boots, ice and roller skate supports, racquet sports equipment, and bicycle wheels, kitchen utensils, toys, and photographic equipment, as well as in a variety of other consumer applications. Examples of food packaging film uses include but are not limited to packaging for meats and cheese and cooling and heating bags and pouches. Examples of filaments include but are not limited to brush bristles, fishing line, sewing thread and filter screens. These polymeric products are also useful for producing blow-molded articles such as bottles, fuel tanks, automotive bumpers, and the like. Other uses for these polymeric products include but are not limited to heat resistant and solvent resistance engineering thermoplastics, medical devices, and electrical insulators. They may be formed into sheet, film, rod, profile, molded, co-extruded, or complex parts by any known plastics processing technique, and can be painted, dyed, decorated, metallized, or coated with abrasion resistant coatings and the like.

The following examples, in which all temperatures are in degrees Celsius and all parts and percentages are by weight unless otherwise indicated, are given for the purposes of illustration only.

#### **Example 1: Preparation of Polymeric Additive:**

##### **Step 1A. Preparation of Rubbery Polymer Latex**

A stainless steel autoclave with an agitator and several entry ports was charged with a mixture of 3.4 parts of acetic acid in 6700 parts of deionized water; 499 grams of a butadiene/styrene copolymer having a composition of approximately 70% butadiene and 30% styrene, and having a particle size of 70  $\mu\text{m}$ ; and 24 parts of sodium formaldehyde sulfoxylate. The autoclave was then evacuated and 6000 parts butadiene, 2000 parts butyl acrylate, 132 parts of sodium dodecyl sulfonate in 1092 parts of water, and 72 parts of tertiary butyl hydroperoxide were added, and heated to 80-85 °C for a period of 8 hours. At the end of the reaction period, no further pressure drop was observed. The residual pressure was vented and the latex was strained to remove gum.

##### **Step 1B. Preparation of a Graft Polymer**

11813 parts of the latex prepared in sept A was heated to 80 °C. 4.1 parts of sodium formaldehyde sulfoxylate was dissolved in 238 parts of deionized water and then added to the 80 °C latex. While maintaining the temperature at 80 °C, 1326 parts of methylmethacrylate, 102 parts of acryloxy propionic acid, 68 parts of butyl acrylate, 2.7 parts of sodium dodecyl sulfonate in 1486 parts deionized water, and 6.8 parts tertiary butyl hydroperoxide were added, and held at 80 °C for one hour. To complete the reaction, an additional 2 parts sodium formaldehyde in 102 parts deionized water, and 3.4 parts tertiary butyl hydroperoxide were added.

##### **Step 2A. Preparation of the Stabilizer Package**

10 grams of octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (hereinafter designated as P1), 10 grams of ethylene bis(oxyethylene) bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate (hereinafter designated as P2), and 30 grams of pentaerythritol ( $\beta$ -laurylthiopropionate) (hereinafter designated as S) were charged to a reaction vessel while heating to 70 °C. When the mixture began to melt (55-60 °C), it was vigorously agitated to yield a homogenous melt. 40.6 grams of sodium dodecyl benzene sulfonate were charged as a 25% active aqueous solution. The emulsion was agitated for 5 minutes, and 9.4 grams of deionized water was added to the emulsion. After an additional 20 minutes of mixing, the emulsion of the stabilizer component was used for preparing the stabilized polymer additive as described in step 2B below.

##### **Step 2B. Preparation of Stabilized Polymeric Additive**

Sixteen grams of the stabilizer component emulsion formed in Step 2As, was added to 1000 grams of the 40% solid polymeric additive latex, synthesized in Step 1. The resulting stabilized polymeric additive was agitated for 20 minutes at 60 °C, and then cooled to less than 40 °C. The emulsion was isolated by freeze drying, and can also be isolated by salt coagulation or spray drying, to provide a polymeric additive which contains 2% stabilizer.

#### **Example 2 - Comparison of Thermal Gravimetric Analysis of Neat Modified Stabilizer Packages in a Polymeric Additive**

TABLE 2

THERMAL GRAVIMETRIC ANALYSIS (TGA) OF POLYMERIC ADDITIVE		
	Polymeric Additive (Package)	TGA In air, 550°F, Time to 10% WtLoss
A)	Unstabilized	10 seconds
B)	P1/P2/S 0.8/0/1.2	36 seconds
C)	P1/P2/S 0/0.8/1.2	6.8 minutes
D)	P1/P2/S 0.4/0.4/1.2	28.3 minutes

Comparison of the TGAs of Stabilizer Packages in Polymeric Additives C and D in air at 550°F (vs. Stabilizer Packages in Polymeric Additives A and D) confirm that there is an unexpected effect caused by the addition of both P1 and P2.

#### Example 3 - Comparison of DSC of Stabilized Polymeric Additives

The polymer products are prepared by compounding a polymeric matrix with a stabilized polymeric additive on an American Leistritz twin screw extruder. Other extruders of various sizes can be used and will afford similar results. (The barrel temperature settings for zones 2-5 were respectively 245, 255, 260, 265 °C.; the gauge (vacuum) pressure was 29 in.; the amps were 13-17; and the screw speed was 120 revolutions per minute).

The polymer products were molded in a Newbury injection molder. Other molds of various sizes can be used and will afford similar results. During molding, the temperature settings for the feed was 260°C, the compress was 266°C, the metering was 268°C, and the nozzle was 271°C. The stationary and moveable mold temperatures were 107°C. The injection time was 5 seconds; and the injection forward cycle time and cure cycle time were 20 seconds. The injection pressure was 500 psi (pounds per square inch), and the back pressure was 100 psi. Screw speed was 100 revolutions per minute).

The ratios of the three stabilizer components were varied in the polymeric additive. The stabilizer loading was kept constant at 2%, and DSC values were obtained for variations of the ratios of components found in Stabilizer Package D (see Table 3).

TABLE 3

RATIO VARIATIONS OF STABILIZER COMPONENTS IN POLYMERIC ADDITIVE (2% LOADING)				
Polymeric Additive (Blend No.)	S	P1	P2	DSC, 190°C
1	1.3	0.4	0.3	118 min.
2	0.3	1.3	0.4	76
3	0.4	0.3	1.3	16
4	1.3	0.3	0.4	>120 min.
5	0.3	0.4	1.3	68
6	0.4	1.3	0.3	53
7	0.67	0.67	0.66	120 min.
8	1.45	0.15	0.4	>120 min.
9 (Package D)	1.2	0.4	0.4	>120 min.

Varying the ration of the components when the total stabilizer loading was 2%, demonstrated improved thermal stability occurred when at least 0.67% of S was used. When less than 0.67% S was used (e.g. 0.3, 0.4), thermal stability dropped sharply.

#### Example 4 - High Temperature Molding



Effectiveness of the stabilizer packages in stabilized additive/nylon blends was tested for processing stability at high temperature molding conditions. All blends remained fully ductile under the Notched Izod Impact Test (ASTM D-256), when molded under standard conditions (260-266-268-271 °C). However, at higher molding conditions (temperatures) of 321-327-332-338 °C, only blends 4,6 and 9 retained 100% ductility (see Table 4).

**TABLE 4**  
**Comparison of 1/8" Notched Izod 23° of Blends Molded at**  
**Standard and High Temperature Conditions**

<u>Blend **</u>	<u>Standard Temperature</u> <u>Molding Joules (ft.-lbs/in.)*</u>	<u>High Temperature</u> <u>Molding Joules/</u> <u>m (ft.-lbs/in.)</u> <u>(% ductibility)</u>	
1	640.3± 10.7 (12±0.2)	533.6± 245.5 (10± 4.6)	(66%)
2	587±32(11±0.6)	480.2±202.8 (9±3.8)	(66%)
3	533.6±10.7 (10±0.2)	480.2±213.4 (9±4.0)	(66%)
4	640.3±42.7(12±0.8)	587±69.4(11±1.3)	(100%)
5	587±32(11±0.6)	480.2±176.1 (9±3.3)	(66%)
6	533.6±5.3 (10±0.1)	640.3±58.7(12±1.1)	(100%)
7	587±21.3(11±0.4)	587±160.1 (11±3.0)	(66%)
8	533.6±26.7(10±0.5)	373.5±53.4(7±1.0)	(66%)
9(Package D)	693.7±26.7(13±0.5)	640.3±32(12±0.6)	(100%)

Standard Molding Condition: 260-266-268-271°C

High Temperature Molding Conditions: 321-327-332-338°C

\*All samples molded at standard conditions were fully ductile

\*\* See Table 3 for the ratio of components of Blends 1-9.

#### **Example 5 - Effect of Heat Aging on Stabilized Polymers**

The polymeric products containing stabilized polymeric additives were evaluated for retention of properties after heat aging. Izod bars and plaques were placed on a carousel in a forced air oven for 24 hours at 150 °C. Samples were removed at designated intervals and tested for impact strength.

TABLE 5

1/8" Notched Izod, Joules/m lft.-lbs./in/l 23°C

Stabilizer Study - Oven Aging at 150°C)

Blend	0 Hrs	4 Hrs	8 Hrs	16 Hrs	20 Hrs	24 Hrs
1	640.3[12](100)	426.9[8](25)	533.6[10](100)	320.2[6](0)	320.2[6](0)	480.2[9] (100)
2	586.7[11](100)	533.6[10](100)	533.6[10](100)	586.7[11](100)	533.6[10](100)	533.6[10](100)
3*	533.6[10](100)	533.6[10](100)	586.7[11](100)	480.2[9] (100)	373.5[7](50)	266.8[5](0)
4	640.3[12](100)	480.2[9] (100)	426.9[8](75)	533.6[10](100)	480.2[9] (100)	533.6[10](100)
5	586.7[11](100)	480.2[9] (100)	480.2[9] (100)	533.6[10](100)	533.6[10](100)	533.6[10](100)
6*	533.6[10](100)	533.6[10](100)	426.9[8](75)	426.8[8](75)	373.5[7](50)	266.8[5](0)
7	586.7[11](100)	586.7[11](100)	586.7[11](100)	533.6[10](100)	480.2[9] (100)	480.2[9] (100)
8	533.6[10](100)	480.2[9] (100)	480.2[9] (100)	- no data -	- no data -	480.2[9] (100)
9	693.7[13](100)	533.6[10](100)	480.2[9] (100)	480.2[9] (100)	533.6[10](100)	533.6[10](100)

2% Stabilizer Loading

American Leistritz Extrusion : 245-255-260-265-265°C

Molding: 260-217°C

( ) = % ductibility

\* = became brittle

**Example 6 -Yellowness Index**

The plaques from the heat aging were evaluated for yellowness index (according to ASTM D-1925). The Notched Izod Test was conducted according to ASTM -D256. After 24 hrs., Blend 9 (Package D) experienced the least amount of colour change of all the variants.

TABLE 6

Yellowness Index of Heat Aged Plaques

Blend	0 hrs.	4 hrs.	8 hr.	16 hrs.	20 hrs	24hrs.
1	15.79	30.07	39.60	66.65	72.10	73.84
2	17.51	31.23	48.91	66.41	70.99	73.15
3	19.13	48.46	53.26	79.63	84.74	89.15
4	19.16	29.71	39.43	54.29	59.70	59.06

5	19.92	30.70	38.37	64.08	17.21	71.04
6	19.71	32.53	39.94	61.05	74.51	67.23
7	19.35	28.34	36.77	61.92	71.10	71.35
8	← -	- -	no data	- -	- -	→
9*	23.54	31.27	36.07	49.68	50.64	51.47
10	(* = Package D)					

#### Example 7- Determination of Effective Stabilizer Level

After determining that Package D (P2/P1/S- 0.4/0.4/1.2) imparted the best thermal stability, stabilizer loading was varied from 1 to 3%, and the ratio of components in Package D (P2/P1/S) were kept the same. DSC testing of the neat modifier was conducted, and 1.0% and 1.5% loadings did not significantly improve thermal stability, while 2.0% loading greatly improved thermal stability. Greater stability was also achieved at 2.5% and 3.0% loadings (see Table 7).

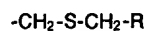
TABLE 7

DSC of Stabilized Polymeric Additive	
Stabilizer Loading	DSC. 190° Max Peak
0%	1 min.
1%	5 min.
1.5%	8 min.
2.0%	110 min.
2.5%	>120 min.
3.0%	>120 min.

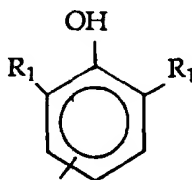
Stabilizer loading of 2% is preferred and found to be the most cost effective.

#### Claims

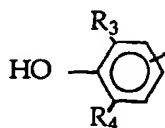
1. A stabilizer composition comprising: 1) sulfide having one or more of the following sulfide groups:



wherein R is (C<sub>1</sub> to C<sub>20</sub>)-alkyl or alkyl alkanoate; or 2,4-bis(n-octylthiol)-6-(4'-hydroxy-3',5'-di-tert-butylanilino)-1,3,5-triazine, and 2) sterically hindered phenol containing one or more sterically hindered phenol groups having the formula:



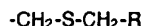
wherein R<sub>1</sub> is a branched chain alkyl, and 3) less sterically hindered phenol containing one or more sterically hindered phenol groups having the formula:



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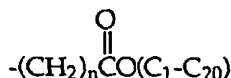
wherein  $R_3$  is hydrogen or  $(C_1-C_4)$ -alkyl, and  $R_4$  is a branched chain alkyl.

- 10 2. A composition as claimed in Claim 1 wherein the phenol (2) comprises from 5 to 40% preferably 8 to 33%, by weight, phenol (3) comprises from 10 to 70%, preferably 15 to 33%, by weight, and sulfide (1) comprises from 15 to 80%, preferably 33 to 73%, by weight, of the total of components 1, 2 and 3.
3. A composition as claimed in Claim 1 or 2 wherein  $R_1$  is branched chain  $(C_4-C_{12})$ -alkyl, preferably tert butyl, 2,2-dimethylpropyl, 1-methylpropyl, sec-propyl, 1,2,2-trimethylpropyl; 2-methylpropyl or 1,2-dimethyl-2-ethylbutyl.
4. A composition as claimed in any preceding claim wherein  $R_4$  is branched chain  $(C_4-C_{12})$ -alkyl, preferably tert-butyl, 2,2-dimethylpropyl, 1-methylpropyl, sec-propyl, 1,2,2-trimethyl propyl, 2-methylpropyl or 1,2-dimethyl-2-ethyl butyl, and  $R_3$  is hydrogen or straight chain  $(C_1-C_4)$ -alkyl.
- 20 5. A composition as claimed in any preceding claim



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wherein R is alkyl, of from 1 to 11, preferably 7 to 11 carbon atoms, or

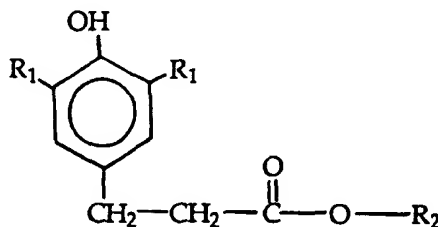


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preferably  $(CH_2)_n CO(C_{12}-C_{18})$  wherein n is 0,1 or 2.

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6. A composition as claimed in any preceding Claim wherein the sulfide is pentaerythritol tetrakis ( $\beta$ -laurylthiopropionate), dilaurylthiodipropionate, pentaerythritol tetrakis (octyl thiopropionate), distearyl thiodipropionate, dimyristyl thiodipropionate, 2,4-bis (n-octylthio)-6-(4'-hydroxy-3',5'-di-tert-butylanilino)-1,3,5-triazine, trimethylolpropane tris(octylthiopropionate), trimethylolmethane tris(octylthiopropionate), ethylene glycol bis(laurylthiopropionate) or didodecylmonosulfide.
- 40 7. A composition as claimed in any preceding Claim wherein phenol (2) has the formula:

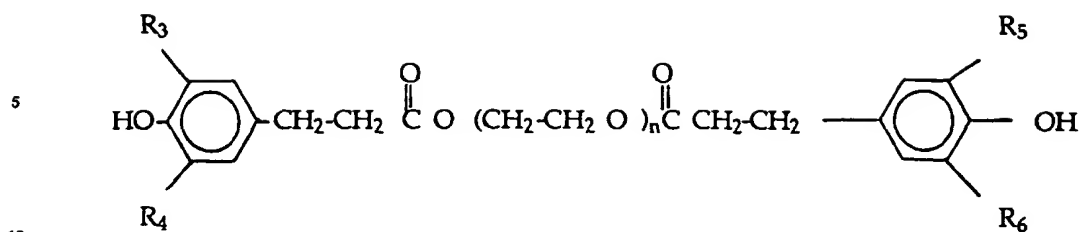


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55 wherein  $R_2$  is an alkyl of at least four carbon atoms, preferably  $(C_4-C_{30})$ -alkyl, more preferably  $(C_{16}-C_{20})$ alkyl.

8. A composition as claimed in any preceding Claim wherein phenol (3) has the formula (IV):



wherein n is an integer of from 1 to 10, R<sub>3</sub> and R<sub>5</sub> are hydrogen or (C<sub>1</sub>-C<sub>4</sub>)alkyl and R<sub>4</sub> and R<sub>6</sub> are branched chain alkyl, preferably as defined for R<sub>4</sub> in Claim 4.

- 15
9. A composition as claimed in any preceding Claim which comprises (a) octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, (b) ethylene bis(oxyethylene) bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate), and (c) pentaerythritol tetrakis ( $\beta$ -laurylthiopropionate), preferably in a weight ratio of 8 to 33 parts (a), 15 to 33 parts (b) and 33 to 73 parts (C), more preferably about 20 parts (a), about 20 parts
- 20
- (b) and about 60 parts (c).

10. A polymer composition comprising polymer and a stabilizer composition, as claimed in any preceding claim, preferably in an amount of from 1 to 3% by weight of the weight of the polymer.

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11. A composition as claimed in Claim 10 wherein the polymer comprises acrylate or methacrylate polymer, a polymer of styrene and/or styrene derivative with acrylate and/or methacrylate and/or maleate and/or fumarate, an olefin copolymer with acrylate and/or methacrylate and/or aromatic polyester and/or maleic acid and/or anhydride, preferably a composition comprising MBS and/or AIMS octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, pentaerythritol tetrakis ( $\beta$ -laurylthiopropionate) and ethylene bis(oxyethylene) bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate).
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12. A polymer product, which maybe a shaped article such as transportation or automotive part, computer housing, appliance handle or housing, electrical or electronic part, telecommunication part, industrial machine part, consumer product, power tool housing, food packaging, wire and cable jacketing, filament, tough film, bottle, fuel tank, automotive bumper, medical device, or other sheet, film, rod, profile or molded part, comprising a polymer matrix and a polymer composition as claimed in Claim 10 or 11 preferably wherein the polymer matrix comprises aromatic polyester, poly(butylene terephthalate), nylon polymer, poly(hexamethylene adipamide), poly(p-phenylene sulfide), polysulfone, polyarylate, polystyrene, poly(ether imide), polyimide, poly(glutarimide), poly(phenylene ether and/or polycarbonate.
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European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 91 31 0470

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 107 617 (CIBA-GEIGY)  * page 2, line 6 - line 9 * * page 3, line 10 - line 23 *	1, 3-4, 6, 8	C08K5/00 //(C08K5/00, 5:13, 5:13, 5:37)
Y	DD-A-264 931 (VEB BUNA) * page 2, line 1 - line 8 * * claim 1 *	1	
Y	DE-A-1 793 708 (CIBA-GEIGY) * page 2, line 1 - page 3, line 15 * * page 7, line 9 - line 11 * * page 7, line 14 - line 18 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08K C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 MARCH 1992	Examiner SIEMENS T.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  A : member of the same patent family, corresponding document			